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VIBRATION AND DISSOCIATION COUPLING BEHIND STRONG SHOCK WAVES

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ABSTRACT

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The coupling between vibrational relaxation and dissociation is discussed. A model for computations of dissociation behind strong shock waves is presented. It is shown that the loss of vibrational energy during dissociation introduces an inverse temperature dependence into the observed dissociation rate of O_2 between 4000 and 8000°K. Changing the model so that dissociation from higher vibrational levels is enhanced results in a dissociation-incubation time immediately behind the shock. The vibrational-energy distribution behind the shock is calculated, and shown to depart considerably from a Boltzmann distribution. The molecular model, which uses a Boltzmann distribution, is shown to give the same result as the non-Boltzmann model for both the nonequilibrium dissociation rate and the dissociation incubation time.

AUTHOR

INTRODUCTION

The rate at which chemical relaxation occurs behind strong shock waves has an important effect on the flow field around high-speed missiles and re-entering space vehicles.^{1,2} The analysis of this complex gasdynamic-

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thermochemical problem has led to numerical methods of solution utilizing high-speed computers. Duff³ reported original calculations for coupled chemical reactions behind normal shock waves, and since then several computer programs have been developed for various chemical-aerodynamic flow problems.⁴⁻⁸ In all cases the machine computations require such models for the chemical processes as will provide a tractable form for the equations and at the same time include the important features of the chemical kinetics. In the present report, a model to represent molecular dissociation at the high speeds associated with superorbital re-entry is described.

The chemical reaction rate constants for molecular dissociation have, in the main, been obtained experimentally at temperatures up to about 8000°K.² Recently experimental dissociation rates for O₂ in an argon atmosphere at temperatures up to ~ 18,000°K have been reported.⁹ In general, however, it is necessary to extrapolate chemical rates up to translational temperatures as high as 50,000°K in order to calculate flows around vehicles traveling at velocities of 40,000 ft/sec. Throughout this high temperature range the times for vibrational and dissociational relaxation are comparable, thus the dissociation process is strongly coupled to the vibrational relaxation.⁹ This problem has been widely discussed in the literature (cf. Refs. 10-12). The relative probability of dissociation from the various vibrational levels becomes important, since the dissociation rate is strongly dependent on the molecular population in excited vibrational levels. It appears likely that a Boltzmann distribution of population in the vibrational levels would not exist, so there arises the serious question of the effect this would have on the calculated dissociation rate.

In the present paper two of the important aspects of molecular dissociation

are discussed. The first concerns the effect of vibrational-dissociation coupling on the measured dissociation rate. Secondly, the distribution in vibrational energy states during the dissociation process, the extent of departure of this distribution from a Boltzmann distribution, and the effect of this departure on the calculated dissociation rates will be discussed.

VIBRATION-DISSOCIATION COUPLING

For a detailed analysis of the coupling of vibrational relaxation with the dissociation rate, an assumption is required concerning the transition probabilities for the excitation of vibration by collision. The Landau-Teller¹³ model of the simple harmonic oscillator with weak interactions was used. This gives transitions only between adjacent states, with the transition probability proportional to the quantum number of the upper state. Without dissociation, this model results in the simple relaxation equation for the energy of the oscillator, the vibrational energy increasing toward its local equilibrium value in an exponential manner with a half life τ_v ;

$$\frac{d\epsilon}{dt} = \frac{\epsilon(T_T) - \epsilon}{\tau_v} \quad (1)$$

where ϵ is the average energy of the vibrators and $\epsilon(T_T)$ is the average energy they would have at the translational temperature T_T .

The use of Eq. (1) at temperatures higher than those where measurements were performed is open to question for several reasons. For example, the calculations of Shuler and Zwanzig,¹⁴ using an impulsive interaction between molecules, show that for this case the 1-quantum selection rule is violated for

high-energy interactions.¹⁵ Again, at high temperatures, the possibility of exchange reactions could shorten the vibrational relaxation time considerably.¹⁶ However, the calculations presented here use the energy relaxation equation to describe the addition of vibrational energy by collisions. At temperatures higher than those at which τ_v has been measured, the value has been extrapolated according to the relation¹³

$$\frac{1}{\tau_v} = 1.2 \times 10^{-9} T^{1/6} \left[1 - \exp\left(-\frac{2228}{T}\right) \right] \exp\left[-\frac{1.04 \times 10^7}{T^{1/3}}\right] [Ar] \quad (2)$$

The constants given in Eq. (2) are those for the vibrational relaxation of O_2 in an argon atmosphere as determined by Camac¹⁷ for the temperature range 1200°K to 7000°K.

To describe the problem of vibrational relaxation in the presence of molecular dissociation, Eq. (1) has been modified with additional terms to account for the drain of vibrational energy by dissociation. This modified equation, which is fully discussed in Ref. 18, can be written:

$$\frac{d\epsilon}{dt} = \frac{\epsilon(T_r) - \epsilon}{\tau_v} - \frac{[\bar{E}(T_r, T_v) - \epsilon]}{[X]} \left(\frac{d[X]}{dt} \right)_f + \frac{[\bar{E}(T_r, T_r) - \epsilon]}{[X]} \left(\frac{d[X]}{dt} \right)_r \quad (3)$$

where $[X]$ is the concentration of the dissociation species, $\left(\frac{d[X]}{dt} \right)_f$ is the rate at which the molecules are dissociating, and $\left(\frac{d[X]}{dt} \right)_r$ is the rate at which the molecules are being formed during recombination. $\bar{E}(T_r, T_v)$ is the average energy lost by vibration in a dissociation and $\bar{E}(T_r, T_r)$ is the average energy gained in a recombination. T_v is the vibrational temperature, the temperature corresponding to a Boltzmann distribution of vibrational energy

ϵ .

As shown in Refs. 18 and 19, the additional terms due to dissociation keep the vibrational temperature below the translational temperature until final equilibrium. This is similar to an evaporation process -- the more energetic vibrators being lost to dissociation. Behind a normal shock wave where the translational temperature stays reasonably constant, for example a shock-tube experiment with a large amount of inert diluent, a situation is reached where the collision processes are feeding energy into the vibrational mode at the same rate as it is being removed by dissociation. Under these conditions the vibrational temperature reaches a plateau considerably below the translational temperature and remains at this lower value until dissociation is almost complete -- i.e. until recombination becomes important. This is illustrated for an oxygen-argon mixture in Fig. 1, taken from Ref. 19. The Camac and Vaughn²⁰ dissociation rate was used in the calculation; i.e.

$$k_f = 3.6 \times 10^{18} T^{-1} \exp\left[-\frac{59380}{T}\right] \frac{\text{cm}^3}{\text{mole-sec.}} \quad (4)$$

Shown in Fig. 1 are computed temperatures -- vibrational and translational -- behind a normal shock in 96% argon, 4% O₂ moving at 2.56×10^5 cm/sec. It is seen that the vibrational relaxation distance is of the order of a few mm, and the dissociation distance some 12 cm. Yet the vibrational temperature is less than the translational temperature during the entire dissociation time because of the very effective removal of vibrational energy by dissociation.

The disparity between vibrational and translational temperatures depends on the relative rates of dissociation from the various vibrational levels. Throughout the work in the present paper, two models of molecular dissociation are considered. In the first, it is assumed that recombination occurs to all

vibrational levels at the same rate -- i.e. in terms of dissociation -- it is assumed that dissociation can occur from all vibrational levels with equal probability in a sufficiently energetic collision. This model is referred to as the non-preferential model. Secondly -- what is probably a more realistic description -- a "preferential" model, where it is assumed that recombination occurs preferentially to the upper levels, and thus dissociation in sufficiently energetic collisions occurs preferentially from the upper levels. The probability distribution used is an exponential one, and is discussed in detail in Ref. 21. The exponential form chosen for the present calculations changes by a factor of about 300 between the top and bottom vibrational levels. It was felt that this represented a reasonably heavy weighting of the upper vibrational levels. All of the calculations presented herein have been performed for both of these models -- non-preferential and preferential -- to illustrate the importance of this feature in the dissociation model. The calculation presented in Fig. 1 was performed with the non-preferential model. A corresponding calculation with the preferential model gives a similar result, except that the vibrational temperature reaches a lower plateau. This is a direct result of the higher relative probability of dissociation from the upper vibrational levels, which permits more vibrational energy to be lost in each dissociation.

The fact that the vibrational temperature is lower than the translational temperature during this entire dissociation period means that the measured dissociation rate will be decreased below the value that would be expected if the vibrational mode were in local equilibrium. Again, the amount that the dissociation rate is affected depends on the model used. For the preferential model the dissociation rate is lower than for the non-preferential model for two reasons: the vibrational temperature is kept lower, which decreases the

dissociation rate and the fact that dissociation from the lower states is unlikely makes this model more sensitive to the lower vibrational temperature. The actual dissociation rate constant can be calculated, by a relation which depends on the number of molecules in each vibrational level -- i.e. that depends on the vibrational temperature. For the non-preferential model this relation is the one used by Hammerling et al.⁴ For the preferential dissociation model it is a simple extension of this.²¹ However, the introduction of the additional terms in the vibrational relaxation equation (3) which keeps the vibrational temperature down during dissociation, makes this coupling very important in changing the dissociation rate. The effect on the dissociation rate for oxygen for these two models is shown as a function of translational temperature in Fig. 2.

Shown in Fig. 2 is the ratio of the forward dissociation rate that would be measured in the plateau region shown in Fig. 1 to the dissociation rate that would obtain if vibration were in thermal equilibrium, plotted vs. the translational temperature behind the shock. The upper curve is the result for the "non-preferential" model, and the lower is for the "preferential" model. These curves represent the solution to some relatively simple equations¹⁹ -- i.e. machine solutions are not required -- which result from equating the first two terms on the right side of Eq. (3). The parameter that determines the solution is the ratio of the measured vibrational relaxation time to the measured dissociation relaxation time. In these calculations the measurements of Camac¹⁷ and Camac and Vaughn²⁰ between 4000 and 8000°K were used, and extrapolated with Eqs. (2) and (4) to the temperatures of interest in the present paper. It can be seen from Fig. 2 that either model introduces a temperature dependence to the dissociation rate between 4000 and 8000°K; a T^{-1} dependence for the non-preferential model and $T^{-3.5}$ dependence for the preferential

model. At higher temperatures, however, this dependence does not continue since for sufficiently energetic collisions appreciable dissociation can originate from the low vibrational levels. The extreme temperature dependence predicted by the preferential model, which has not been observed in dissociation rate experiments, seems to imply that the exponential chosen for this model weights the upper levels more heavily than should be done.

These considerations then show that the experimentally determined rate constants, k_f , should be divided by the factor shown in Fig. 2 to obtain the value of $k_{f,eq}$, for purposes of calculating reverse rate constants or for extrapolation to higher temperatures. It is clear that the observed inverse temperature dependence should not be extrapolated above about 10,000°K.

EFFECT OF NON-BOLTZMANN DISTRIBUTION IN VIBRATION

In the consideration of vibrational nonequilibrium a Boltzmann-like distribution of vibrational energy has been assumed in the two models discussed previously. Thus it has been possible to define a vibrational temperature based on the total vibrational energy, which has greatly simplified the calculation. One would expect that under the extreme temperature conditions discussed, that departures from this Boltzmann distribution may occur. To investigate the seriousness of this departure, the large capability of the normal-shock computer program to handle many coupled chemical reactions has been utilized. This capacity permits a detailed description of the relaxation of a fictitious molecule with as many as 18 vibrational levels. Each of these 18 vibrational levels has been considered a separate molecule, coupled to other molecules through the vibrational transition probabilities, and each molecule capable of

dissociation with a specified chemical rate. The number of each of the 18 species present can then be used to observe how much the distribution departs from Boltzmann. A somewhat similar calculation for H_2 has been reported by Pritchard.¹² For the present case the results, especially for the over-all dissociation rate, can be compared with those obtained from the much simpler programs previously discussed, as applied to the 18 level molecule. This comparison can then reasonably be accepted as a proper comparison for molecules such as O_2 and N_2 which may have several times more vibrational levels.

With the recombination rate taken equal for each of the 18 levels, the results can be compared with the non-preferential model, and with the rates for the upper levels properly weighted, results can be compared with the preferential model. For the dissociation and vibration relaxation rates, and the dissociation energy, values equal to those for O_2 were chosen for the 18 level molecule to keep the temperature range of interest the same. To inspect the populations of the vibrational levels a "population factor" has been defined by the relation that the number of molecules in a vibrational level n_v , divided by the number in the ground level, n_0 , has an exponential dependence on the ratio of the energy E_v of the vibrational level v to the population factor. Thus $\frac{n_v}{n_0} = \exp - \left(\frac{E_v}{k \Theta_v} \right)$ where Θ_v is the population factor for the v^{th} vibrational level. Then in a Boltzmann distribution, all Θ_v would be equal, and would be equal to the vibrational temperature.

The results of several calculations for a strong shock ($T_f \sim 17,000^\circ K$) are shown in Fig. 3. If the dissociation rate is taken as zero, all the values of Θ_v are equal as expected from the theorem for a simple harmonic oscillator,²² i.e. the distribution relaxes to final equilibrium through a series of

Boltzmann distributions. This is denoted in the upper curve labeled T_v (no dissociation). The reverse rate constant for the reaction between the (i) and ($i-1$) vibrational levels is expressed as $k_{r,i,i-1} = (i) k_{r,1,0}$ where

$$k_{r,1,0} = \frac{1}{z_v} \frac{1}{(1 - e^{-\omega/kT})} \quad (5)$$

For the present calculations, the z_v value as expressed in Eq. (2) was used. However, if dissociation occurs, the reactions for dissociation from each vibrational level must be included. The result shown for the 18-level molecule utilizes a preferential dissociation from the upper levels, with the recombination rate constant for each level given as

$$k_{r,i} = k_r \frac{e^{v\omega/kU}}{\sum_{v=0}^{17} e^{v\omega/kU}} \quad (6)$$

where k_r is the equilibrium recombination rate constant for the molecule, and was computed from Ref. 20 as

$$k_r = 3 \times 10^{15} T^{-1/2} \frac{\text{cm}^6}{\text{mole}^2 \cdot \text{sec.}} \quad (7)$$

The term U is a constant which describes the preferential recombination to upper levels. For the non-preferential model, $U = \infty$, and all recombination rates $k_{r,i}$ are equal. For the preferential model, the value of U has been taken as $1/6 D/k$ where D is the dissociation energy of O_2 . This weights the recombination rate of the uppermost level approximately three hundred times as heavily as that of the ground level. As shown in Fig. 3, the resulting values of θ_v for the various levels are different and reach different plateaus

during the quasi-equilibrium zone, indicating a non-Boltzmann distribution. In the calculation where a Boltzmann distribution is assumed, the value of the vibrational temperature, shown by the lower solid line in Fig. 3, is seen to be in the region of the Θ_v values for the upper vibrational levels. This is due to the fact that the preferential model is used in this example, where most of the dissociation occurs from the top-most levels. It should be noted that a similar calculation was done for the case of the non-preferential dissociation, and there is still a broad spread in the values of Θ_v , but the vibrational temperature obtained from the Boltzmann calculation is closer to the Θ_v value for $v = 8$. Corresponding calculations for weaker shocks giving a translational temperature of 6000°K, give very similar results.

Since T_v follows the Θ_v values of the important dissociating levels, the dissociation rate calculated from the Boltzmann model is very close to the total dissociation rate from the 18 separate levels of the non-Boltzmann model. This can be seen in Fig. 4. The dissociation rates for each of the levels reaches a plateau in the same way as the population factors shown in Fig. 3. The sum of these rates, which is the measured rate, is also shown in Fig. 4. It is compared with the rate calculated under the assumption of a Boltzmann distribution, and it can be seen that the agreement is excellent.

The direct effect on the number of molecules remaining behind a shock wave for three different calculations is shown in Fig. 5. Results for the preferential model are shown for both Boltzmann and non-Boltzmann calculations. These values are proportional to the negative of the integral of the values in Fig. 4, and are seen to be very nearly equal. The non-preferential model gives a larger dissociation rate corresponding to the larger negative slope in Fig. 4. It is of interest to observe the "incubation time" or lag time in oxygen

dissociation given by the preferential dissociation model for both the Boltzmann and non-Boltzmann models. During this "incubation time", dissociation is greatly inhibited by the lack of population of the higher vibrational levels. Observed incubation times of the order of the extrapolated vibrational relaxation time have been reported by Wray⁹ for test conditions similar to those shown in Fig. 5.

SUMMARY

Within the confines of the Landau-Teller model of vibrational energy relaxation, with additional terms to account for vibrational energy loss due to dissociation, it has been demonstrated that an inverse temperature dependence is introduced into the dissociation rate for O_2 in the range from 4000 to 8000°K. A model wherein it is assumed that all vibrational levels have equal probability of dissociation in a sufficiently energetic collision yields approximately a T^{-1} dependence in this region. A model with preferential dissociation from upper levels -- an exponential distribution of probability with the upper level weighted about three hundred times greater than the lower gives a stronger dependence -- approximately $T^{-3.5}$ and seems inconsistent with measured results. In both cases this calculated temperature dependence disappears above 8000 or 10,000°K. The preferential dissociation model predicts a dissociation-incubation time comparable with the vibrational relaxation time, as is observed in dissociation experiments by Wray.⁹ Thus there are two types of experimental data which can lead to a determination of the proper weighting of dissociation rates from the upper levels. However, sufficient experimental data for this determination are not as yet available.

In view of the importance of the assumption of a Boltzmann distribution in the previous calculations, the departure from this distribution was investigated. The relaxation of a simple harmonic oscillator with 18 vibrational levels was calculated numerically, permitting a non-Boltzmann distribution in the vibrational levels. These results were compared with calculations which assume a Boltzmann distribution. It was found that the Boltzmann calculation gives an excellent description of the dissociation rate, although the actual distribution is quite non-Boltzmann. Thus it appears that the Boltzmann model, which provides a much more tractable set of equations for shock calculations, may be adequate for aerodynamic flow calculations behind strong shock waves.

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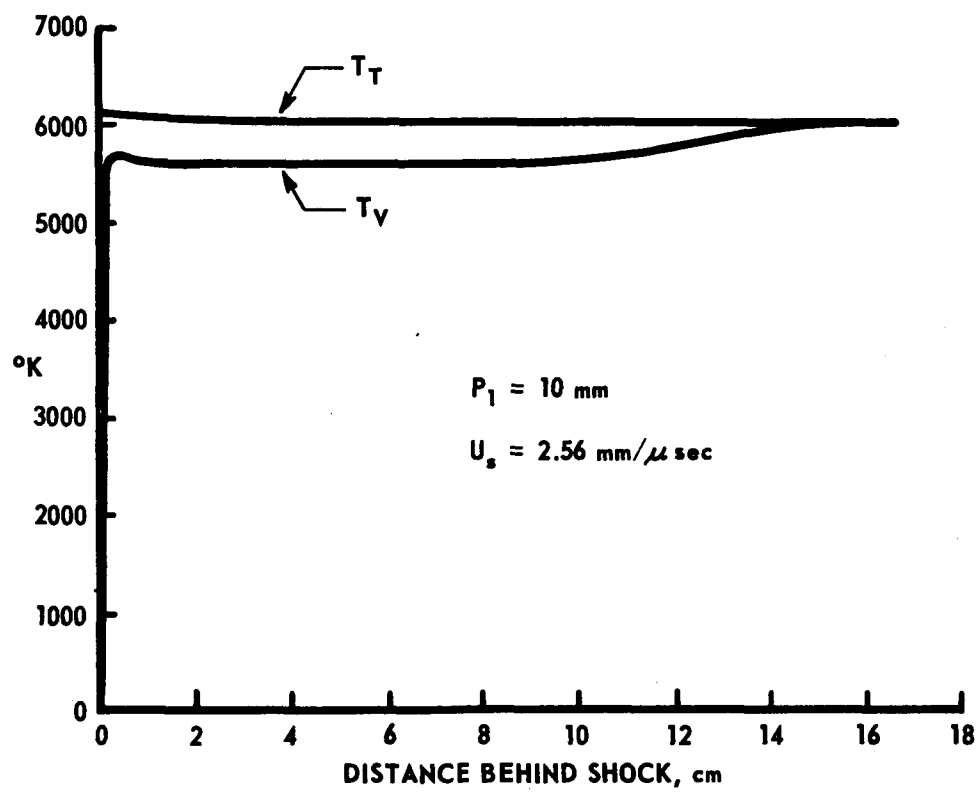


Figure 1 TEMPERATURE HISTORY BEHIND NORMAL SHOCK IN 96% Ar - 4%O₂

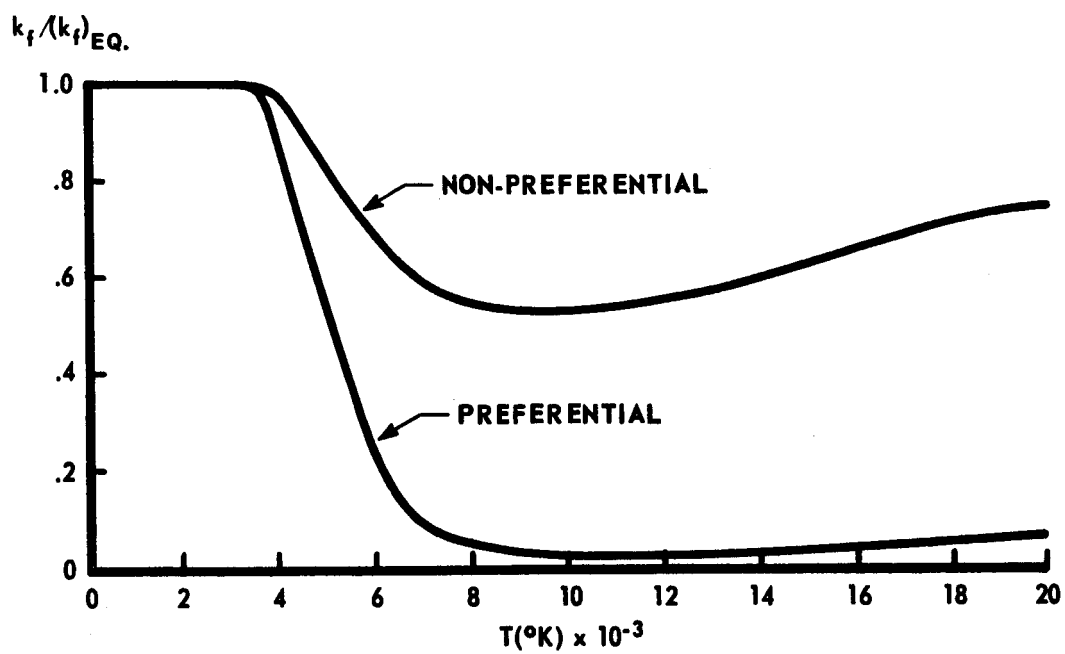


Figure 2 EFFECT OF VIBRATIONAL NON-EQUILIBRIUM
ON DISSOCIATION RATE CONSTANT

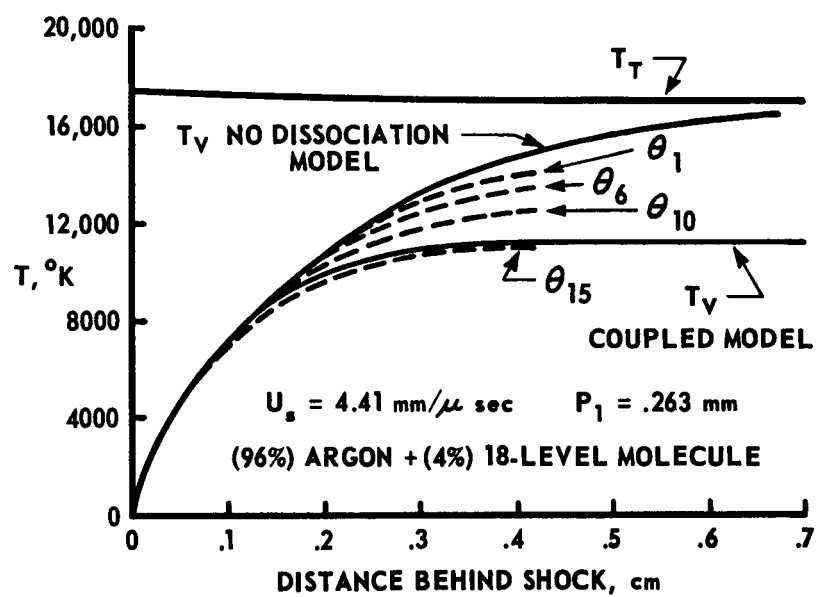


Figure 3 VIBRATIONAL RELAXATION WITH PREFERENTIAL DISSOCIATION FROM UPPER LEVELS

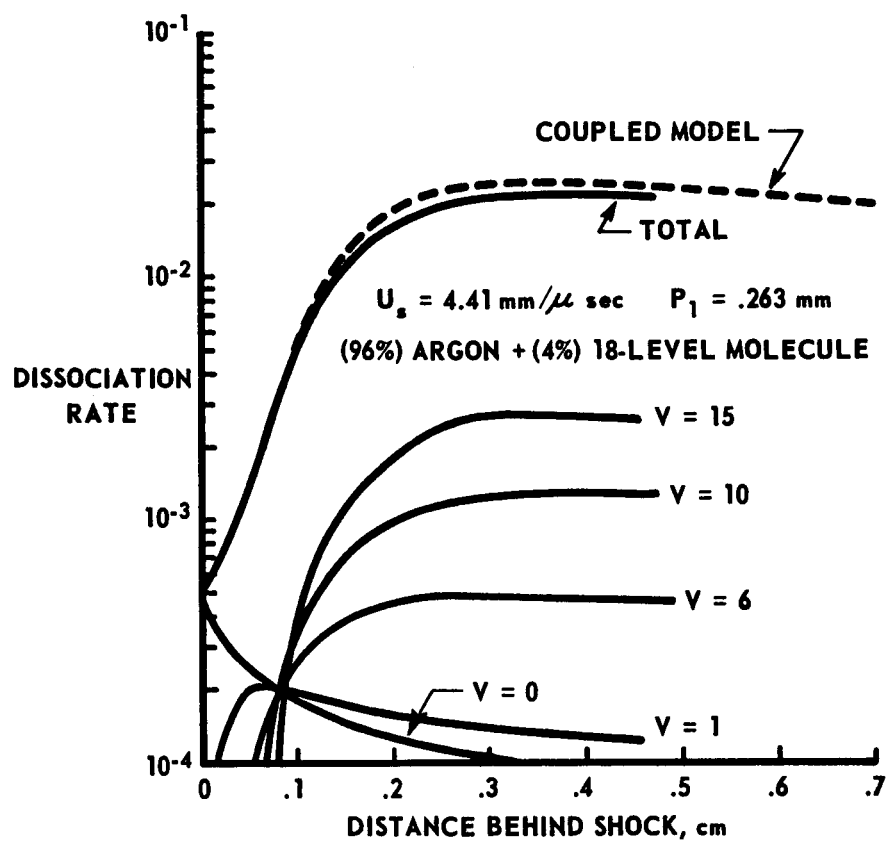


Figure 4 DISSOCIATION RATE FROM VIBRATIONAL LEVELS OF 18-LEVEL MOLECULE

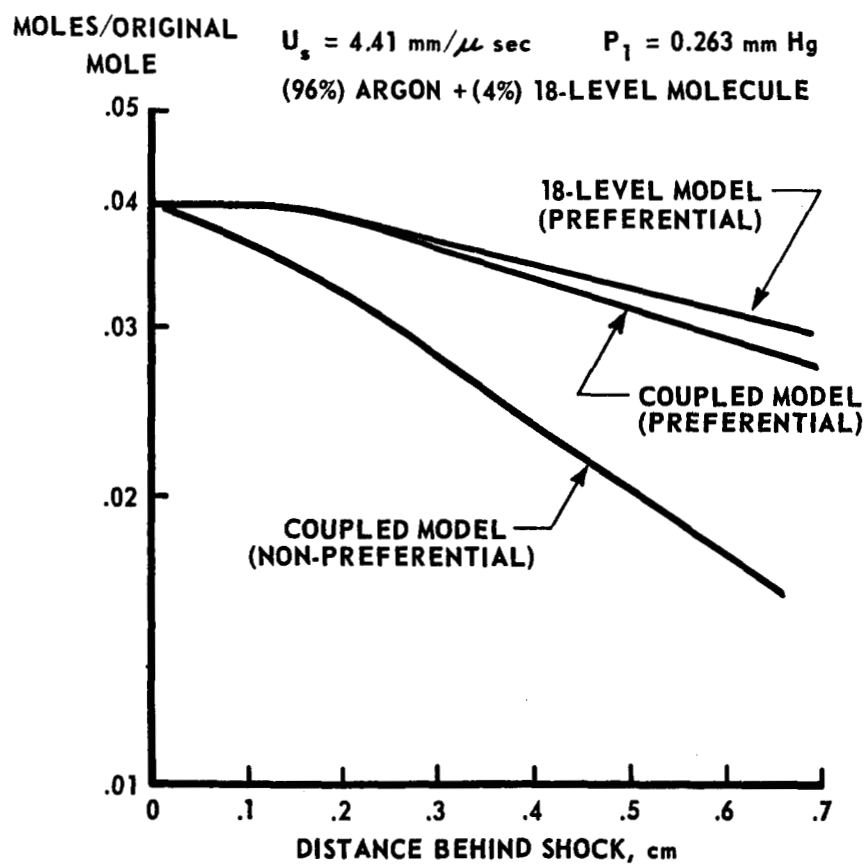


Figure 5 MOLECULE CONCENTRATION BEHIND NORMAL SHOCK